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# SUBSOLIDUS STRUCTURE OF THE SYSTEM $Al_2O_3 – SiO_2 – MgO – P_2O_5$ (A REVIEW)

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The structure of the $Al_2O_3 – SiO_2 – MgO – P_2O_5$ system in the subsolidus range is analyzed. Splitting of the system into elementary tetrahedra is shown, their volumes and degrees of asymmetry are calculated, a topological graph of relationships between the tetrahedra is constructed, and a geometrical-topological characteristic of phases in the considered system is given. Eutectic temperatures, as well as compositions and conode lengths, are calculated for some pseudobinary and ternary sections. Ranges of the system compositions suitable for fire-resistant ceramic technology and for heat-insulating materials are specified.

Research into refractory and ceramic materials and their structure and properties is impossible without understanding phase equilibria in multicomponent systems of high-melting nonmetallic and silicate materials. The majority of binary and some ternary systems are described in detail in the reference literature [1 – 5] and serve as physicochemical basis for the development of important materials for contemporary engineering.

The four-component system $Al_2O_3 – SiO_2 – MgO – P_2O_5$ (hereafter the following abbreviations are used: A for $Al_2O_3$, S for $SiO_2$, M for MgO, and P for $P_2O_5$) contains such compounds as cordierite, enstatite, forsterite, mullite, $Al_2O_3$, $SiO_2$, and MgO used in special and engineering ceramics, mainly refractories. Some compounds can be used as phosphate binders, for instance, $M_3P$, $AP_3$, AP, SP, etc. Therefore, this system is interesting as a basis for producing some ceramic and refractory materials with phosphate binders.

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Based on analysis of published data [1, 6, 7] we previously assumed the existence of three silicophosphates: $S_2P$, $S_3P_2$, and SP [8, 9]. Studies of the compounds in the S – P system using contemporary methods of analysis (x-ray phase, IR spectroscopy, microscopic, chemical) [10, 11] revealed that the stable compounds in this system are silicon oxymonophosphate $Si_5O[PO_4]_6$ ($S_5P_3$) and diphosphate $SiP_2O_7$ (SP), whereas compounds $S_2P$ and $S_3P_2$, which we believed to exist, are in fact a mechanical mixture of phases $SiO_2$ with $Si_5O[PO_4]_6$ and $Si_5O[PO_4]_6$ with $SiP_2O_7$, respectively. Therefore, in splitting the systems containing the binary subsystem S – P we hereafter took into account phases $S_5P_3$ and SP.

Among the ternary systems the best studied one is the system M – A – S, in which four binary and two ternary (cordierite and sapphirite) compounds are identified. In view of the great importance of the compositions in this system, intense research into some of its segments continues, especially the cordierite – corundum – mullite – spinel area

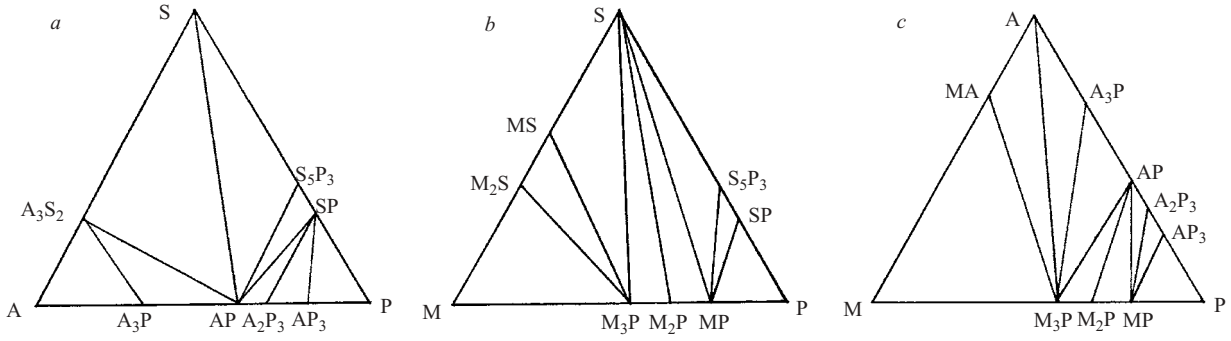


**Fig. 1.** Triangulation of systems A – S – P (*a*), M – S – P (*b*), and M – A – P (*c*).

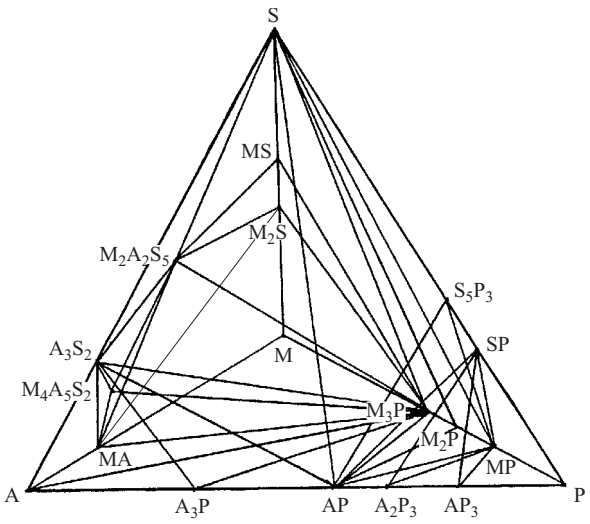


**Fig. 2.** Tetrahedral splitting of system A – S – M – P.

[12, 13]. We have accepted the variant of the system described in [14]. Systems A – S – P and M – S – P are studied in less detail, mainly in areas with a low content of $P_2O_5$ (up to 50%). Taking into account confirmation of the existence of phases $S_5P_3$ and SP and the data of [8, 9], the triangulation of these ternary system is presented in Fig. 1*a* and *b*. The structure of the M – A – P subsystem is investigated in [15 – 17], and its full splitting taking into account the data in [18] is shown in Fig. 1*c*.

Despite the fact that many compositions in the system are widely used in practice, this system is not fully studied and its subsolidus structure has not been discovered in the literature. The purpose of the present study is to investigate the subsolidus structure of the system M – A – S – P.

The following conjugate reaction takes place in the system area adjacent to conode S – $A_3S_2$:

$$9M_2A_2S_5 + 6AP = 8A_3S_2 + 29S + 6M_3P,$$

for which the temperature dependence of free Gibbs energy variation was calculated using the source data from [2, 19, 20]:

$$\Delta G_t = – 1{,}781{,}483.4 – 42.45T \text{ (J/mole)}.$$

A thermodynamic analysis of the reaction [21, 22] indicated that compounds $M_2A_2S_5$ and AP interreact, whereas $A_3S_2$, S, and $M_3P$ do not react and form a "filled contour." Hence it follows that the considered region is split into two elementary tetrahedrons: AP – S – $M_3P$ – $A_3S_2$ and $A_3S_2$ – S – $M_3P$ – $M_2A_2S_5$.

Thus, considering the available data, the system M – A – S – P in the subsolidus region is analyzed taking into account 4 oxides and 13 binary and two ternary compounds, which leads to splitting of the system into 19 elementary tetrahedra (Fig. 2). The conode lengths and the elementary tetrahedron volumes were calculated taking into account barycentric coordinates and Euclidean elements, and the liquidus surface was estimated using the Epstein – Howland formula [23] based on earlier developed programs [12, 20]. The elementary tetrahedra and their volumes of existence and degrees of asymmetry are represented in Table 1.

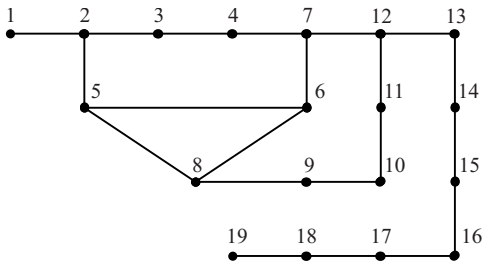


**Fig. 3.** Topological graph of relationships between the elementary tetrahedra in the quaternary system A – S – M – P.

To study the relationship of elementary tetrahedrons, a topological graph was constructed (Fig. 3), for which the number of edges equal to 21 was calculated. The graph is "flat," without "false" edge intersections, and ""nested' tetrahedra are absent. The system has 21 combinations of three phases that do no directly ensue from the component ternary subsystems.

The geometrical-topological characteristics of the phases in the system phase is given in Table 2. The phases S, $M_3P$, $A_3S_2$, AP, and $M_2A_2S_5$ have the highest probability of existence, which suggests the technological advisability of using these phases of the specified system.

As follows from Table 1, the highest relative volumes are occupied by tetrahedra AP – S – $M_3P$ – $A_3S_2$ (No. 12), M – MA – $M_3P$ – $M_2S$ (No. 1), and MA – $M_2S$ – $M_3P$ – $M_2A_2S_5$ (No. 2). Eutectic temperatures and degrees of asymmetry were calculated for these tetrahedra, which amounted

**TABLE 1**

| No. | Elementary tetrahedra of system A – S – M – P | Volume, ‰ | Degree of asymmetry |
|---|---|---|---|
| 1 | M – MA – $M_3P$ – $M_2S$ | 165.2 | 1.678 |
| 2 | MA – $M_2S$ – $M_3P$ – $M_2A_2S_5$ | 113.9 | 1.620 |
| 3 | $M_2S$ – MS – $M_3P$ – $M_2A_2S_5$ | 32.3 | 3.643 |
| 4 | MS – S – $M_3P$ – $M_2A_2S_5$ | 75.6 | 2.753 |
| 5 | MA – $M_4A_5S_2$ – $M_3P$ – $M_2A_2S_5$ | 10.1 | 2.753 |
| 6 | $M_4A_5S_2$ – $A_3S_2$ – $M_3P$ – $M_2A_2S_5$ | 35.2 | 4.147 |
| 7 | $A_3S_2$ – S – $M_3P$ – $M_2A_2S_5$ | 53.4 | 2.681 |
| 8 | MA – $M_4A_5S_2$ – $M_3P$ – $A_3S_2$ | 11.1 | 5.631 |
| 9 | MA – A – $M_3P$ – $A_3S_2$ | 43.1 | 3.074 |
| 10 | A – $A_3P$ – $M_3P$ – $A_3S_2$ | 41.1 | 3.074 |
| 11 | AP – $A_3P$ – $M_3P$ – $A_3S_2$ | 34.4 | 2.796 |
| 12 | AP – S – $M_3P$ – $A_3S_2$ | 192.2 | 1.975 |
| 13 | AP – S – $M_3P$ – $M_2P$ | 40.9 | 8.895 |
| 14 | AP – S – $M_2P$ – MP | 59.0 | 6.448 |
| 15 | AP – S – $S_5P_3$ – MP | 54.2 | 2.538 |
| 16 | AP – $S_5P_3$ – SP – MP | 10.7 | 3.576 |
| 17 | AP – $A_2P_3$ – SP – MP | 6.2 | 3.845 |
| 18 | $A_2P_3$ – $AP_3$ – SP – MP | 8.6 | 2.383 |
| 19 | $AP_3$ – P – SP – MP | 12.8 | 1.539 |

**TABLE 2**

| No. | Phase | Number of tetrahedra in which it is present | Number of phases with which it coexists | Existence volume, ‰ | Probability of existence, ‰ |
|---|---|---|---|---|---|
| 1 | A | 2 | 4 | 84.3 | 0.0211 |
| 2 | S | 6 | 8 | 475.3 | 0.1188 |
| 3 | M | 1 | 3 | 165.2 | 0.0413 |
| 4 | P | 1 | 3 | 12.7 | 0.0032 |
| 5 | MA | 5 | 7 | 343.5 | 0.0859 |
| 6 | $M_2S$ | 3 | 5 | 311.4 | 0.0778 |
| 7 | MS | 2 | 4 | 107.9 | 0.0270 |
| 8 | $M_3P$ | 13 | 12 | 848.6 | 0.2121 |
| 9 | $M_2P$ | 2 | 4 | 99.9 | 0.0250 |
| 10 | MP | 6 | 8 | 151.4 | 0.0379 |
| 11 | $A_3S_2$ | 7 | 8 | 410.6 | 0.1026 |
| 12 | $A_3P$ | 2 | 4 | 75.5 | 0.0189 |
| 13 | AP | 7 | 9 | 397.6 | 0.0994 |
| 14 | $A_2P_3$ | 2 | 4 | 14.8 | 0.0037 |
| 15 | $AP_3$ | 2 | 4 | 21.3 | 0.0053 |
| 16 | $S_5P_3$ | 2 | 4 | 65.0 | 0.0162 |
| 17 | SP | 4 | 6 | 38.2 | 0.0096 |
| 18 | $M_2A_2S_5$ | 6 | 7 | 320.5 | 0.0801 |
| 19 | $M_5A_5S_2$ | 3 | 4 | 56.3 | 0.0141 |
| | Total | – | – | 4000.0 | 1.0000 |
| | Maximum | 13 | 12 | 848.6 | 0.2121 |
| | Minimum | 1 | 3 | 12.7 | 0.0032 |

**TABLE 3**

| Conode A – B | Eutectic temperature, K | | Conode length, ‰ |
|---|---|---|---|
| | calculated | experimental | |
| $A_3S_2 – M_3P$ | 1630 | – | 741 |
| $M_2A_2S_5 – M_3P$ | 1626 | – | 625 |
| $M_3P$ – S | 1562 | 1603 | 867 |
| AP – $M_3P$ | 1618 | – | 441 |
| AP – S | 1833 | – | 870 |
| AP – $A_3S_2$ | 2065 | – | 504 |
| $M_2A_2S_5$ – S | 1757 | 1738 | 435 |
| $M_2A_2S_5 – A_3S_2$ | 1821 | 1738 | 323 |
| $A_3S_2$ – S | 1931 | 1860 | 718 |

to 1551, 1593, and 1499 K and 1.97, 1.67, and 1.62, respectively.

The characteristics of some pseudobinary and ternary sections of the system M – A – S – P are shown in Tables 3 and 4.

Analysis of the obtained data shows that the ternary sections considered have a relatively low degree of asymmetry (not more than three), and mixtures based on these compositions are technologically convenient with respect to the accuracy of component proportioning. Sections $A_3S_2$ – S – AP and $A_3S_2$ – S – $M_2A_2S_5$ reach the surface of the concentration tetrahedron M – A – S – P and the others pass in a 3D space.

The tetrahedra AP – S – $M_3P$ – $A_3S_2$, MA – $M_2S$ – $M_3P$ – $M_2A_2S_5$ and M – MA – $M_3P$ – $M_2S$ have a low degree of

**TABLE 4**

| Section A – B – C | Estimated eutectic temperature, K | Molar composition of eutectic, % | | | Degree of asymmetry |
|---|---|---|---|---|---|
| | | A | B | C | |
| $M_3P – S – A_3S_2$ | 1562 | 56.7 | 43.2 | 0.1 | 1.207 |
| $M_3P$ – S – AP | 1551 | 51.8 | 42.1 | 6.1 | 1.975 |
| $M_3P – A_3S_2$ – AP | 1618 | 91.1 | 0.1 | 8.8 | 1.682 |
| $A_3S_2$ – S – AP | 1823 | 2.5 | 74.8 | 22.7 | 1.726 |
| $M_3P$ – S – $M_2A_2S_5$ | 1561 | 56.2 | 43.1 | 0.8 | 1.997 |
| $M_3P – A_3S_2 – M_2A_2S_5$ | 1626 | 96.9 | 0.1 | 3.0 | 2.691 |
| $A_3S_2$ – S – $M_2A_2S_5$ | 1756* | 1.0 | 66.0 | 33.0 | 2.221 |

* According to [14] it is equal to 1713 K.

asymmetry and substantial relative volumes, and considering estimated eutectic temperatures, the composition ranges of these tetrahedra are suitable for producing heat-resistant ceramic and heat-insulating materials that are widely used in various sectors of industry,

The data on the structure of the system $Al_2O_3 – SiO_2 – MgO – P_2O_5$ obtained by us are needed for further research into the development of new technologies of composite, reinforced, and fibrous products and for increasing efficiency in using traditional materials.

## REFERENCES


1. *Phase Diagrams of Silicate Systems* [in Russian], Nauka, Leningrad, Issue 1 (1969), Issue 3 (1972), Issue 4 (1974).
2. A. S. Berezhnoi, *Multicomponent Oxide Systems* [in Russian], Naukova Dumka, Kiev (1970).
3. A. S. Berezhnoi, *Multicomponent Alkaline Oxide Systems*, Naukova Dumka, Kiev (1988).
4. E. M. Levin, C. R. Robbins, and H. F. McMurday, "Phase Diagrams for Ceramics," in: *Amer. Ceram. Soc., Vols. 1 – 3*, Washington (1964 – 1975).
5. *Minerals, A Reference Book, Phase Diagrams, Issues 1 and 2* [in Russian], Nauka, Leningrad, (1974).
6. T.-Y. Tien T.-Y. and F. A. Hummel, "The System $SiO_2P_2O_5$," *J. Am. Ceram. Soc.*, **45**(9), 422 – 424 (1962).
7. A. N. Murashkevich, V. V. Pechkovskii, R. Ya. Mel'nikova, and T. I. Barannikova, "Study of silicophosphates," *Zh. Neorg. Khim.*, **29**(12), 3014 – 3019 (1984).
8. Ya. N. Pitak, "Subsolidus structure of the system CaO – MgO – $SiO_2$ – $P_2O_5$ and its significance in refractory technology," in: *Publ. of UkrNIIO Institute* [in Russian], Karavella, Kharkov (1998), pp. 152 – 158.
9. Ya. N. Pitak, A. O. Nagornyi, and G. N. Shabanova, "Subsolidus structure of the system CaO – $Al_2O_3$ – $SiO_2$ – $P_2O_5$," *Ogneup. Tekh. Keram.*, No. 9, 19 – 21 (1997).
10. A. E. Mal'shikov and I. A. Bondar', "Physicochemical study of the system $SiO_2$ – $P_2O_5$," *Zh. Neorg. Khim.*, **33**(1), 198 – 202 (1988).
11. I. A. Bondar' and A. E. Mal'shikov, *Phosphates of Group IV Elements* [in Russian], Nauka, St. Petersburg (1992).
12. N. M. Bobkova, "Corrections to the phase diagram of the system MgO – $Al_2O_3$ – $SiO_2$," *Steklo Keram.*, No. 10, 11 – 12 (1992).

13. S. M. Logvinkov, G. D. Semchenko, and D. A. Kobyzeva, "Rearrangement of the phase diagram conodes of the system $MgO – Al_2O_3 – SiO_2$ and its technological prospects," *Ogneup. Tekh. Keram.*, No. 11, 4 – 8 (1996).
14. A. S. Berezhnoi, Ya. N. Pitak, A. D. Ponomarenko, and N. P. Sobol', *Physicochemical Systems of High-Melting Nonmetallic and Silicate Materials* [in Russian], UMK VO, Kiev (1992).
15. V. M. Ust'yantsev, M. G. Tretnikova, and L. S. Zholobova, "Subsolidus phase diagram of the system $MgO – Al_2O_3 – P_2O_5$," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **9**(3), 448 – 449 (1973).
16. F. J. Gonzalez and J. W. Halloran, "The Ternary System $MgO – Al_2O_3 – P_2O_5$," *J. Am. Ceram. Soc.*, Nos. 9 – 10, 599 – 600 (1980).
17. E. Yu. Zhukovina, A. S. Berezhnoi, N. V. Gul'ko, and A. M. Gavrish, "Subsolidus structure of the system $MgO – Al_2O_3 – ZrO_2 – P_2O_5$," *Dokl. Akad. Nauk USSR, Ser. B*, No. 9, 43 – 47 (1980).
18. E. Yu. Zhukovina, *Subsolidus structure of the Five-Component System $CaO – MgO – Al_2O_3 – ZrO_2 – P_2O_5$ and Prospects of Using It in the Technology of Refractories, Author's Abstract of Candidate's Thesis* [in Russian], Sverdlovsk (1981).
19. V. I. Babushkin, G. M. Matveev, and O. P. Mchedlov-Petrosyan, *Thermodynamics of Silicates* [in Russian], Sroiizdat, Moscow (1972).
20. Ya. N. Pitak, G. N. Shabanova, and V. V. Taranenkova, "Calculation methods of construction of eutectic system diagrams using computers," in: *Proc. Inter. Sci. Conf. "Computers: Science, Engineering, Technology, and Health"* [in Russian], Mishkol'tz, Kharkov (1993), pp. 142 – 143.
21. Yu. V. Churilova, Ya. N. Pitak, and V. V. Churilov, "Structure of the region $AlPO_4 – Mg_3P_2O_8 – Al_6Si_2O_{13} – SiO_2 – Mg_2Al_4Si_5O_{18}$ in the system $MgO – Al_2O_3 – SiO_2 – P_2O_5$," in: *Vestn. KhGPU, Issue 90* [in Russian] (1999), pp. 49 – 51.
22. N. V. Pitak, Ya. N. Pitak, L. V. Serova, et al., "Structure of the section $Al_6Si_2O_{13} – SiO_2 – Mg_3P_2O_8$ in the liquidus range," *Publ. of KhGPU Institute, Issue 6, Part 3* [in Russian] (1998), pp. 143 – 145.
23. L. F. Epstein and W. H. Howland, "Binary Mixture of $UO_2$ with other Oxides," *J. Am. Ceram. Soc.*, **36**(10), 334 – 337 (1953).